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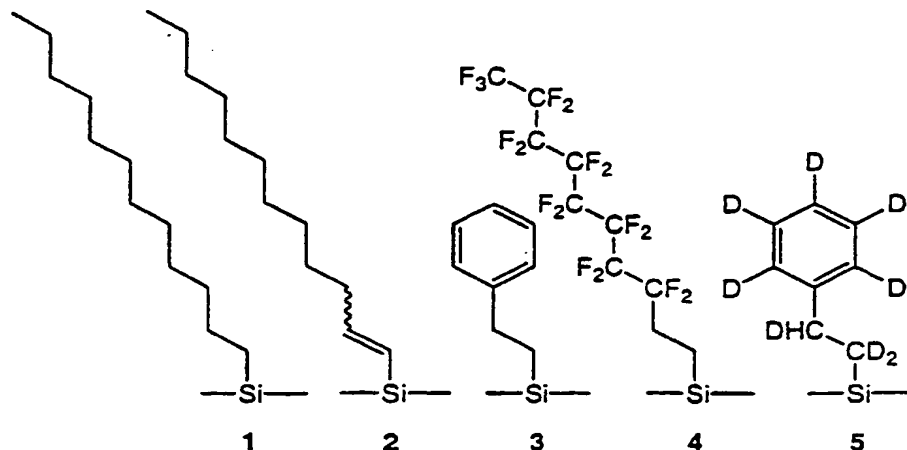
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(54) Title: FUNCTIONALIZED POROUS SILICON SURFACES



(57) Abstract: The present invention is directed to porous silicon substrates having a monolayer covalently bounded to a surface of the silicon substrates and a method for forming such substrates. The method of forming a covalently bound monolayer on porous silicon surfaces comprising the steps of photoactivating a porous silicon surface and contacting the surface with an alkene or alkyne.

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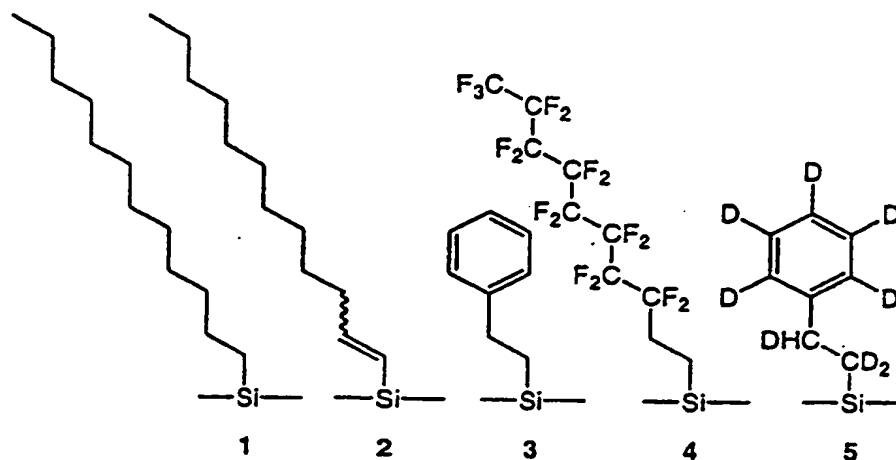
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(54) Title: **FUNCTIONALIZED POROUS SILICON SURFACES**

(57) Abstract

The present invention is directed to porous silicon substrates having a monolayer covalently bound to a surface of the silicon substrates (1, 2, 3, 4, 5) and a method for forming such substrates. The method of forming a covalently bound monolayer on porous silicon surfaces comprising the steps of photoactivating a porous silicon surface and contacting the surface with an alkene or alkyne.



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FUNCTIONALIZED POROUS SILICON SURFACES

Field of the Invention

This invention relates to surface functionalized porous silicon
5 substrates. More particularly, this invention is directed to porous silicon surfaces
having covalently bound monolayers formed by a light induced hydrosilylation reaction
between the porous silicon surface and optionally substituted alkenes and alkynes.

Background and Summary of the Invention

10 Silicon surface chemistry is of fundamental technical significance
because of the ubiquitous role of silicon in modern technology, and yet it is only just
beginning to be investigated. Virtually all microprocessor chips in electronic products
are based upon crystalline silicon wafers. Control of silicon surface chemistry is crucial
to allow access to technologically interesting thin films for fabrication of new
15 electronic devices.

In 1990, Canham and co-workers showed that silicon wafers could be
etched using hydrofluoric acid to produce a microns-thick porous layer (termed porous
silicon) that exhibits photoluminescence upon exposure to UV light [Canham, L. T.
Appl. Phys. Lett. 1990, 57, 1046]. Potential applications for porous silicon include
20 uses as chemical sensors, biosensors, optoelectronic devices such as electroluminescent
displays, photodetectors, and as a matrix for photopumped tunable lasers. As a result,
modification and characterization of photoluminescent porous silicon surfaces has
become an area of intense interest. The surface of porous silicon is populated with Si-
H_x bonds (x = 1,2,3), exposed Si-Si bonds, and defects such as open valence,
25 "dangling" Si atoms. The porous silicon material is composed of this surface,
sublaminal nanocrystalline Si, and 55-95% empty space.

Recent developments in the functionalization of porous silicon have
enabled Si-C bonds to be formed on the porous-Si surface by attacking the weak Si-Si
bonds of exposed nanocrystalline submaterial with Grignard or alkyllithium reagents.
30 Grignard and alkyllithium transmetallation and the use of Lewis acid catalysis have also
been used to exploit the great population of surface Si-H bonds. Thermal, radical-

-2-

mediated, and UV photolytic alkene hydrosilylation has also been reported for flat Si and Si hydride surfaces.

The present invention is directed to a new one step method of efficiently functionalizing the porous Si surface through light promoted hydrosilylation of unsaturated carbon-carbon bonds.

Brief Description of the Drawings

Fig. 1 Surfaces prepared through white light promoted hydrosilylation on porous Si.

Fig. 2 Transmission FTIR spectra of surfaces 1, 2, and 3, prepared at 22 mW cm⁻², 44 mW cm⁻², and 44 MW CM-2 light intensity, respectively, for 60 minutes.

Fig. 3 Incorporation versus light intensity for 1-dodecyne hydrosilylation on porous Si. The peak intensity of the V_{as}(CH₂) vibration at 2925 cm⁻¹ was used to determine incorporation levels. Because different samples were prepared for each data point, each was normalized with respect to the V (Si-H_x) peak intensity at 2100 cm⁻¹ before the hydrosilylation reaction in order to compare absolute intensities of V_{as}(CH₂).

Fig. 4 Photoluminescent (PL) spectra of freshly etched porous Si (dotted line), followed by 60 minute hydrosilylation reaction at 22 mW cm⁻² white light with 1-dodecene (surface 1, solid line).

Fig. 5a Generalized procedure for functionalizing a porous silicon surface with two different substrates having functional groups R and R'', respectively.

Fig. 5b A porous silicon surface functionalizing with phenethyl and dodecyl.

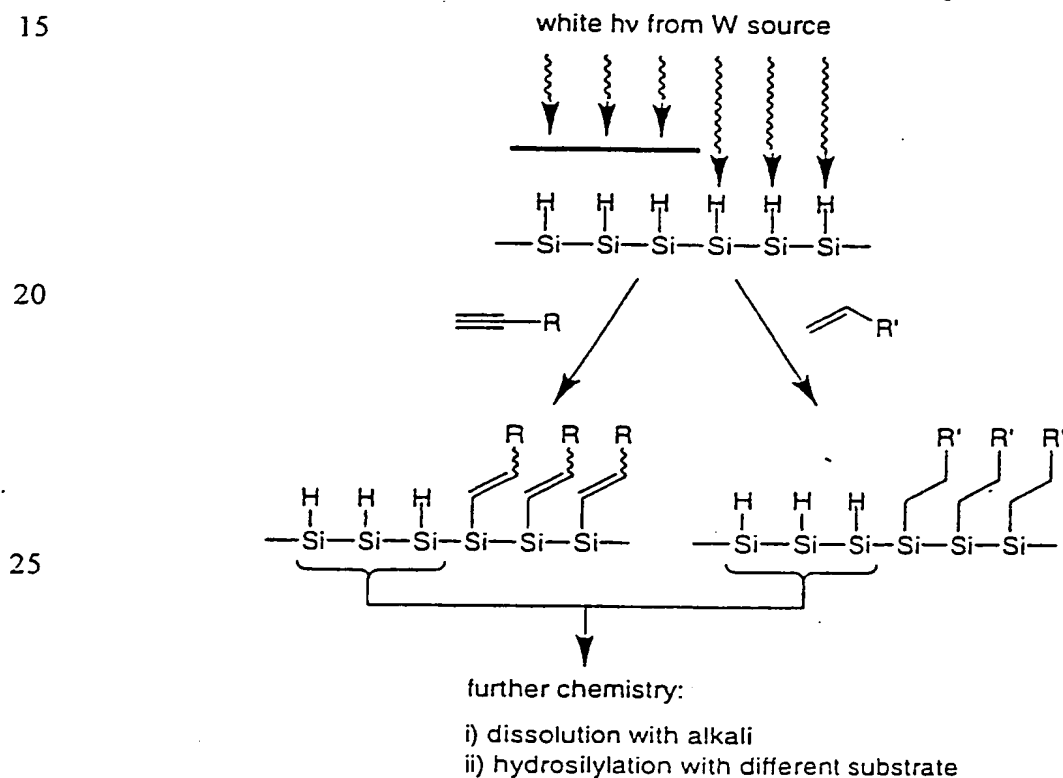
Detailed Description of the Invention

Hydrosilylation of olefins and alkynes has been known to proceed under a wide variety of reaction conditions. Late transition metal catalysts were commonly used in these reactions; however, such catalysts have the potential for activating the weaker Si-Si bonds on the surface (bond strengths: Si-Si = 340 kJ/mol, Si-H = 393 kJ/mol). Lewis acid catalyzed/mediated hydrosilylation reactions have also been

reported. Aluminum chloride, for example, is known to be an effective catalyst for hydrosilylation of both alkynes and alkenes, but that Lewis acid is not soluble in non-polar solvents and, therefore, is not suitable for solid phase chemistry. The Lewis acid EtAlCl_2 is soluble in non-polar solvents and can be used for hydrosilylation of readily available alkynes and alkenes, however these acids eliminate the photoluminescence of the porous silicon surface and thus such procedures are not useful for preparing optoelectronic devices.

This invention provides a mild and general method for covalent modification of the surface of porous silicon through hydrosilylation of readily available alkynes and alkenes mediated by a light-directed methodology that substantially retains the original photoluminescence of the original porous silicon surface. The alkynes and alkenes react with surface bound Si-H groups to yield surface bound vinyl and alkyl groups, respectively, as outlined in scheme 1.

Scheme 1. White light promoted hydrosilylation on porous Si.



30 In accordance with the present invention a method for preparing functionalized silicon surfaces for use in optoelectronic devices is described. In one embodiment a covalently bound monolayer is formed on a porous silicon substrate

having a surface comprising silicon hydride groups and exhibiting photoluminescence. The method comprises the step of contacting the porous silicon substrate with an amount of an optionally substituted C_2 - C_{24} alkene or optionally substituted C_2 - C_{24} alkyne sufficient to form the monolayer on the surface of the silicon substrate, and
5 illuminating the silicon surface in the presence of the optionally substituted C_2 - C_{24} alkene or optionally substituted C_2 - C_{24} alkyne.

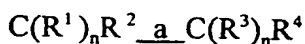
In one preferred embodiment the porous silicon surface is illuminated with white light (having a wavelength ranging from about 400-700 nm) using a light source that provides an intensity ranging from about 0.22 to about 44 mW cm⁻². The
10 role of the white light is believed to generate Si radicals due to either cleavage of weak Si-H bonds on the surface or to produce photogenerated holes on the surface which are subsequently attacked by alkyne or alkene nucleophiles. Illumination of the silicon hydride groups in the presence of the unsubstituted or substituted C_2 - C_{24} alkene or unsubstituted or substituted C_2 - C_{24} alkyne results in the hydrosilylation of the alkenes
15 or alkynes, so that a monolayer is covalently bound to the surface of the silicon substrate. Advantageously, this reaction allows for substantial retention of the photoluminescence of the original porous silicon surface. In one preferred embodiment the step of illuminating comprises exposing the silicon substrate to emissions from a Tungston ELH light source. Preferably the silicon substrate is
20 illuminated while in the presence of the alkene or alkyne, however the silicon substrate can be illuminated prior to contact with the alkene or alkyne.

Hydrosilylation of alkynes and alkenes catalyzed by photoactivation of surface situated silicon hydride groups on a porous silicon surface yields vinyl and alkyl groups, respectively, covalently bound to the surface. The present method is tolerant
25 of a variety of functional groups. Thus, for example, nitrile, hydroxy and methyl ester substituted olefins can be used to form covalently bound monolayers on porous silicon surfaces without additional protecting groups.

This invention also provides porous silicon substrates having a surface comprising a covalently bound monolayer that substantially retains the
30 photoluminescence of the original nonfunctionalized porous silicon substrate. In one embodiment the functionalized porous silicon surface retains greater than 90% of the photoluminescence of the original nonfunctionalized silicon surface. Porous silicon

substrates functionalized in accordance with the present invention are remarkably stable under a wide variety of conditions normally resulting in degradation of the delicate porous surface structure.

In one aspect of this method, the C₂-C₂₄-alkene or C₂-C₂₄ alkyne is a compound of the formula:



wherein

a represents a double or triple bond;

when **a** is a triple bond, **n** is 0;

when **a** is a double bond, **n** is 1; and

R¹, **R**², **R**³, and **R**⁴ independently, are hydrogen, hydroxy, halo, cyano, isocyano, C₁-C₁₈ alkoxy, C₁-C₁₈ carboxy, C₁-C₁₈ alkoxy carbonyl, primary, secondary or tertiary amino, thiol, optionally substituted phosphino, borane (1) or borane (2), or C₁-C₁₈ alkylthioether or an optionally substituted C₁-C₁₈ alkyl, aryl, heteroaryl or vinyl group; and when **R**¹, **R**², **R**³ or **R**⁴ is a substituted group, the group is substituted with one or more substituents selected from the group consisting of hydroxy, halo, cyano, isocyano, C₁-C₁₈ alkoxy, C₁-C₁₈ carboxy, C₁-C₁₈ alkoxy carbonyl, primary, secondary or tertiary amino, thiol, optionally substituted phosphino, borane (1) or borane (2), or C₁-C₁₈ alkylthioether, halo C₁-C₁₈ alkyl, cyano C₁-C₁₈ alkyl, isocyano-C₁-C₁₈ alkyl, C₁-C₁₈ carbamido, or C₁-C₁₈ alkylthio group, a C₁-C₁₈ ferrocene substituent or another electron donor, or a biologically significant ligand selected from an antibody, a receptor protein, DNA or RNA, or a DNA or RNA analog capable of forming a double or triple stranded complex with DNA or RNA; or **R**² and **R**⁴, together with the carbon atoms to which they are attached, form a 5-, 6-, 7- or 8- membered ring.

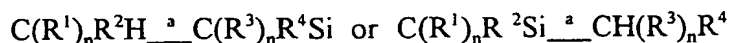
In another embodiment, this invention provides porous silicon substrates having a surface comprising a covalently bound monolayer wherein the photoluminescence of the original porous silicon surface is substantially retained. Porous silicon provides a high surface area, and therefore is uniquely suited for use in sensor construction and electrometric sensing of analytes in test solutions. Porous silicon, however, has been known to be unstable to a wide variety of conditions. The one-step hydrosilylation strategy of the present invention, utilizing white light (0.22-44 mW cm⁻²) to activate porous silicon surfaces in the presence of a variety of alkynes and

alkenes, generates stable surface bound alkenyl and alkyl functionalities which preserves greater than 60%, and more preferably greater than 80%, of the original porous silicon photoluminescence. For example, hydrosilylation of 1-dodecene and 1-dodecyne produces surfaces which preserve 97% and 61% of their original photoluminescence, respectively, and are stable to aerated boiling KOH (pH 10) solution. This strategy makes possible selective photopatterning of the porous Si surface that can be used for Si lithography.

Thus, one advantage of this invention is that it allows formation of a surface-protecting monolayer under relatively mild conditions, i.e., at room temperature (25°C). The invention also provides a method whereby the photoluminescence of the original porous silicon surface is substantially retained. In another embodiment, the methods and compositions of this invention provide for the manufacture of improved biosensors having a biological component that reacts with an analyte in a test solution.

Moreover, porous silicon having a monolayer of covalently bound hydrophobic groups demonstrates remarkable stability. For example, when porous silicon functionalized with hydrophobic groups using this method is subjected to boiling in aerated aqueous KOH (pH 10), no oxidation was seen and only minor changes in the surface IR spectra were noted. When nonfunctionalized porous silicon is subjected to those same conditions, the porous layer dissolves. Because of the high stability displayed by porous silicon surfaces protected in accordance with this invention, this methodology represents an important step towards the use of porous silicon in technologically important applications.

This invention further provides a porous silicon substrate having a surface comprising a covalently bound monolayer wherein the monolayer comprises a group of the formula:



wherein

Si is a surface silicon atom through which the substituted or unsubstituted vinyl or alkyl group is bonded to the silicon surface;
 a represents a single or double bond;
 when a is a double bond, n is 0;

- when a is a single bond, n is 1; and
- R^1 , R^2 , R^3 , and R^4 independently, are hydrogen, hydroxy, halo, cyano, isocyano, C_1 - C_{18} alkoxy, C_1 - C_{18} carboxy, C_1 - C_{18} alkoxy carbonyl, primary, secondary or tertiary amino, thiol, optionally substituted phosphino, borane (1) or borane (2), or C_1 - C_{18} alkylthioether or an optionally substituted C_1 - C_{18} alkyl, aryl, heteroaryl or vinyl group;
- 5 and when R^1 , R^2 , R^3 or R^4 is a substituted group, the group is substituted with one or more substituents selected from the group consisting of hydroxy, halo, cyano, isocyano, C_1 - C_{18} alkoxy, C_1 - C_{18} carboxy, C_1 - C_{18} alkoxy carbonyl, primary, secondary or tertiary amino, thiol, optionally substituted phosphino, borane (1) or borane (2), or C_1 - C_{18} alkylthioether, halo C_1 - C_{18} alkyl, cyano C_1 - C_{18} alkyl, isocyano- C_1 - C_{18} alkyl, C_1 - C_{18} carbamido, or C_1 - C_{18} alkylthio group, a C_1 - C_{18} ferrocene substituent or another electron donor, or a biologically significant ligand selected from an antibody, a receptor protein, DNA or RNA, or a DNA or RNA analog capable of forming a double or triple stranded complex with DNA or RNA; or
- 10 R^2 and R^4 , together with the carbon atoms to which they are attached, form a 5-, 6-, 7- or 8- membered ring.

Preferred aspects of this invention are those porous silicon surfaces wherein a is a double bond, and R^1 , R^2 , R^3 , or R^4 is an aryl or heteroaryl or phosphino metal chelating ligand and any metal complex of this metal chelating ligand.

- 20 Other preferred aspects of this invention are those porous silicon surfaces wherein

1) at least a portion of the covalently bound R^2 or R^3 group comprises a biologically significant ligand; or.

- 2) R^2 is H or C_1 - C_4 alkyl, and R_3 comprises a biologically
- 25 significant ligand.

The term " C_1 - C_x -alkyl" refers to a straight, branched or cyclic alkyl group having the designated (x) number of carbon atoms. It is understood that, if the group is cyclic, it must a minimum of three carbon atoms.

- The term "primary, secondary or tertiary amino" represent an R^5R^6N -
- 30 group wherein R^5 and R^6 , independently, represent a hydrogen, C_1 - C_6 alkyl or an aryl.

The term "optionally substituted phosphino" refers to a group of the formula R^5R^6P - wherein R^5 and R^6 are as defined supra.

The term "optionally substituted borane (1) and borane (2)" refers to a borane (1) or borane (2) group having one or more substituents independently selected from the group consisting of hydrogen, hydroxy, C₁-C₁₂ alkoxy, C₁-C₆ alkyl, thiol and aryl.

5 The terms "aryl" and "heteroaryl" are used as they are understood in the art. Examples of useful aryl groups are benzyl and naphthyl. Heteroaryl groups having one or more hetero-ring atoms, wherein at least one heteroatom is nitrogen are particularly useful in the methods and compositions of this invention. Examples of such groups include pyridyl, pyrrolyl, bipyridyl phenanthrolyl, pyrazinyl and indolyl.

10 The term "DNA or RNA analog" refers to a chemical analog of DNA or RNA having other than a phosphate linked sugar "backbone" that is capable of forming a double stranded complex with DNA or RNA.

 The method of this invention is tolerant of a wide variety of functional groups and porous silicon functionalized with hydrophobic groups using this technique
15 is remarkably stable to adverse conditions, such as boiling aerated water and boiling aqueous KOH (pH 10).

 The method of this invention can also be carried out with mixtures of alkynes and alkenes to provide covalently bound surfaces wherein the mole fraction of the groups in the monolayer correspond generally to the mole fractions of the alkynes
20 and/or olefins in the reagent mixture used to form the monolayer.

 Alternatively, covalently bound monolayers comprising mixtures of covalently bound species can be formed by sequential photopatterning reactions. In accordance with the present invention, photopatterning of alkyl and alkenyl monolayers on porous silicon surfaces is controlled by selective white light illumination
25 of the silicon surface to induce localized hydrosilylation reactions of alkynes and alkenes. In accordance with one embodiment, the silicon surface is contacted with a first alkene or alkyne reactant and a portion of the silicon surface is exposed to a photoactivating light source in a predetermined pattern.

 In one embodiment the selective illumination of the silicon surface is
30 controlled by masking regions from exposure to the light source emissions. Methods of masking the silicon surface from the photoactivating light source are well known to those skilled in the art. The silicon surface is then washed to remove unbound

reactants. The nonfunctionalized silicon hydride groups can be selectively etched with alkaline solutions, leaving the photoluminescent alkyl or alkenyl terminated surface intact, or hydrosilylated with a different substrate. For example, the silicon surface can be contacted with a second alkene or alkyne reactant and again exposed to the photoactivating light source to form a porous silicon surface functionalized with two or more different compounds. In addition, functional groups present on the covalently bound monolayer, e.g., hydroxy, amino, carboxy and thiol, can be used to functionalize the surface further by coupling to biologically significant molecules using standard ester or amide-forming coupling techniques.

In accordance with another embodiment, regiospecific application of the light-promoted hydrosilylation reaction involves alkene or alkyl substitution of the porous Si surface through photopatterning. A white light pattern is focused on a porous-Si sample to which neat liquid alkene or alkyne has been applied. After reaction times of 15 minutes to 12 hours, alkene or alkyl incorporation in the illuminated areas can clearly be identified under photoluminescence conditions. Functionalized regions appear red shifted compared to nonfunctionalized regions for the 1-dodecyne (surface 2) and 1-dodecene (surface 1) reacted surfaces, respectively.

Photopatterning conducted with simple laboratory apparatus involving only an f/75 reducing lens can achieve 40 μm resolution ($25.0 \text{ lines mm}^{-1}$) between light and dark areas from a focused USAF 1951 resolution target. Si lithography can be accomplished by treatment of the photopatterned sample in boiling alkaline KOH (pH 12, 15 seconds) solution, which destroys normal porous-Si J173 but leaves functionalized porous-Si intact.

If functionalized porous Si is to be involved in IC fabrication, minimal process interference would be advantageous. Photoelectronic activation of the porous Si surface to effect functionalization is a one-step reaction which avoids the costs and chemical hazards of using highly active organometallic reagents and, as the amount of heating is negligible, observes a minimal thermal budget.

In order to illustrate the operation of this invention, the following non-limiting examples are provided:

Examples

FTIR spectra were collected using a Perkin-Elmer 2000 spectrometer in transmission mode, typically obtained at 4 cm^{-1} resolution with 16 to 32 scans collected. Reagents obtained from commercial sources were argon sparged and
5 filtered over anhydrous alumina in the glove box before use. Light intensities were measured with a hand-held radiometer (Metrologic).

Porous Si material was prepared from polished crystalline n-type, P-doped, $0.70\text{ }\Omega\text{-cm}$ silicon wafers (Transition Technology International). The etching was carried out with either a 0.28 cm^2 or 1.1 cm^2 area exposed to a 24% HF/24%
10 $\text{H}_2\text{O}/52\%$ ethanol etching solution, 3 minutes at $+71.4\text{ mA cm}^{-2}$ (0.28 cm^2) or $+59.0\text{ mA cm}^{-2}$ (1.1 cm^2) current and approximately 25 mW cm^{-2} white light illumination from a 300 W ELH W bulb (GE). After anodization, the samples were washed with ethanol and blown dry under a nitrogen stream.

Hydrosilylation reactions: Typically, a 0.28 cm^2 etched wafer, still in
15 the etching cell, was brought into the glove box. The substrate was added (100 gL) to the surface directly, followed by the solvent, if necessary (400 μL). A ChemGlass window (borosilicate) was sealed with a Viton O-ring over the etching cell reservoir and clamped. The etching lamp was used as a light source with an intensity of 22.4 mW cm^{-2} at the sample. A thermocouple was assembled with the cell and mounted
20 against the back of the wafer in temperature monitoring experiments. In wavelength-dependent studies, a single-grating monochromator (Bausch and Lomb) was used to isolate wavelengths to approximately 5 nm with approximately 10^{-4} transmittance of extraneous wavelengths.

Photoluminescence (steady state) measurements: An Oriel 250 W
25 mercury arc lamp and a Bausch and Lomb monochromator was set to 440 nm with a 450 nm SWP filter (CVI SPF450) as the excitation source, giving an intensity of 0.2 mW cm^{-2} at the sample. Luminescence was passed through a 490 nm LWP filter (CVI LP490) into an Acton Research Spectra Pro 275 0.275 m monochromator and a Princeton Instruments LN_2 cooled CCD detector, model LN/CCD-1024-E/1.

30 Photopatterning: Light from the etching lamp was passed through a condenser lens onto a mirrored surface and was directed down toward a negative pattern approximately 30 cm total distance from the light source. About 10 cm below

the pattern an achromatic $f/75$ lens was positioned, about 8 cm above the sample on the laboratory jack. The position of the second lens and the jack surface were manipulated to give the best focused pattern visible on the sample with a magnifying glass. All attempts were made to extinguish non-focused light from the sample.

5 One step hydrosilylation of alkenes and alkynes was conducted using white light to activate porous silicon surfaces. The light used for the functionalization is derived from an ordinary tungsten ELH light source of moderate intensity ($0.22\text{--}44\text{ mW cm}^{-2}$). A neat substrate (selected from 1-dodecene, 1-dodecyne, styrene, 1H,1H,2H,2H-perfluorodecyl, and $[D_8]$ Phenethyl, see Fig. 1) was added to the surface
10 under inert atmosphere and the excess washed off after exposure times as short as 15 minutes. FTIR transmission spectra of surfaces prepared through hydrosilylation of 1-dodecene (surface 1), 1-dodecyne (surface 2), and styrene (surface 3) are shown in Fig. 2. Furthermore the degree of incorporation of 1-dodecyne has been demonstrated as dependent upon light intensity at the sample (see Fig. 3), keeping exposure times
15 constant (30 minutes). Low levels of substitution were observed for control experiments in absence of light.

Photoluminescence of the silicon surface, which is essential for optoelectronic applications, is largely retained after functionalization. Surfaces 1 and 2 show an average $97\% \pm 10\%$ and $61\% \pm 10\%$ photoluminescence intensity,
20 respectively, compared to freshly prepared porous Si samples. A red shift of approximately 10 nm is observed in the peak photoluminescence wavelength of functionalized samples as demonstrated in Fig. 4 for surface 1. Surfaces 1 and 2 are chemically stable to treatment in boiling aerated aqueous KOH (pH 10) solution for 30 minutes.

25 Preliminary mechanistic explorations suggest alkene and alkyne hydrosilylation on the surface of porous Si. Using $[D_8]$ styrene as a substrate (surface 5), a molecule with no C-H bonds, hydrosilylation was observed by the appearance of methylene $\nu(\text{CD-H})$ vibrations at 2917 cm^{-1} and 2846 cm^{-1} , indicating transfer of surface hydride to the perdeuterated olefin. Difference transmission FTIR spectra
30 taken before and after hydrosilylation clearly indicate consumption of Si-H groups.

A porous Si sample was functionalized with two different types of substrates by illuminating half of a wafer while treated with neat styrene. After

reaction, excess styrene was washed off, the entire sample treated with 1-dodecene, and the second half exposed to light to produce the functionalized surface shown in Fig. 5. FTIR spectra of the two sides showed almost exclusively phenethyl and dodecyl incorporation, respectively.

- 5 The role of the white light may be to generate Si radicals due to either cleavage of weak Si-H bonds on the surface or to produce photogenerated holes on the surface which are subsequently attacked by alkyne or alkene nucleophiles. That electron deficient alkynes (phenylacetylene, 4-methylphenylacetylene and 4-chlorophenylacetylene) require longer reaction times (12 h) suggests a mechanism
- 10 involving nucleophilic attack. Dangling bonds present on freshly prepared porous silicon can also react with alkenes and alkynes and account for the weak incorporation observed when the hydrosilylation reaction is allowed to proceed in absence of light. Monochromatic light promoted hydrosilylation of 1-dodecyne at 450 nm, 550 nm and 650 nm (1 h, 1.8×10^{15} photons $\text{cm}^{-2} \text{s}^{-1}$) showed decreasing substitution with
- 15 increasing wavelength. Temperature monitoring of the silicon wafer with a thermocouple during the photochemical reaction showed little change (maximum increase of 2°C after 1 h at 22 mW cm^{-2}) during the course of the reaction, indicating that thermal activation is not an important factor. The nature of the solvent had no effect on the degree of incorporation as demonstrated using solutions of 1-dodecyne
- 20 (20%) in hexanes, toluene, CH_2Cl_2 , and 0.1 M $\text{N}(\text{nBu})_4\text{PF}_6/\text{CH}_2\text{Cl}_2$.

- 1H,1H,2H,2H-perfluorodecyl terminated surface (4) IR: $V_{\text{as}}(\text{CH}_2)$ 2921 cm^{-1} , $V_{\text{s}}(\text{CH}_2)$ 2854 cm^{-1} , $V(\text{SiH}_2)$ 2114 cm^{-1} , $V(\text{SiH})$ 2082 cm^{-1} , $\delta_{\text{as}}(\text{CH}_2)$ 1439 cm^{-1} , $\delta_{\text{s}}(\text{CH}_2)$ 1353 cm^{-1} , $V_{\text{as}}(\text{CF}_3)$ 1241 cm^{-1} , $V_{\text{as}}(\text{CF}_2)$ 1204 cm^{-1} , $V_{\text{s}}(\text{CF}_2)$ 1147 cm^{-1} ,
- 25 $V(\text{SiO})$ 1061 cm^{-1} , $\delta_{\text{s}}(\text{SiH}_2)$ 904 cm^{-1} , $\delta(\text{SiH}_2)$ 657 cm^{-1} , $\delta(\text{SiH})$ 682 cm^{-1} .

- [D₈] Phenethyl terminated surface (5) IR: $V_{\text{as}}(\text{CD-H})$ 2917 cm^{-1} , $V_{\text{s}}(\text{CD-H})$ 2846 cm^{-1} , $V(\text{ArD})$ 2273 cm^{-1} , $V(\text{CD}_2)$ 2187 cm^{-1} , $V(\text{SiH}_2)$ 2114 cm^{-1} , $V(\text{SiH})$ 2082 cm^{-1} , $V(\text{Ar C=C})$ 1569 cm^{-1} , $\delta_{\text{as}}(\text{CD-H})$ 1450 cm^{-1} , $\delta_{\text{s}}(\text{CD-H})$ 1323 cm^{-1} , $V(\text{SiO})$ 1105 cm^{-1} ,
- 30 $\delta_{\text{s}}(\text{SiH}_2)$ 907 cm^{-1} , $\delta(\text{SiH}_2)$ 661 cm^{-1} , $\delta(\text{SiH})$ 623 cm^{-1} .

CLAIMS

1. A method for forming a covalently bound monolayer on a porous silicon substrate having a surface comprising silicon hydride groups and exhibiting photoluminescence, said method comprising the step of
 - contacting the porous silicon substrate with an amount of an optionally substituted C_2-C_{24} alkene or optionally substituted C_2-C_{24} alkyne sufficient to form the monolayer on the surface of the silicon substrate;
 - illuminating the surface in the presence of the optionally substituted C_2-C_{24} alkene or optionally substituted C_2-C_{24} alkyne so that the monolayer is covalently bound to the surface of the silicon substrate and the photoluminescence of the surface is substantially retained.
2. The method of claim 1 wherein the step of illuminating comprises exposing the silicon substrate to emissions from a Tungston ELH light source.
3. The method of claim 1 further comprising the step of illuminating a portion of the silicon surface to form a functionalized patterned silicon surface.
4. The method of claim 3 further comprising the step of washing the functionalized patterned silicon surface, contacting the functionalized patterned silicon surface with an optionally substituted C_2-C_{24} alkene or optionally substituted C_2-C_{24} alkyne and illuminating the surface in the presence of the optionally substituted C_2-C_{24} alkene or optionally substituted C_2-C_{24} alkyne.
5. The method of claim 1 or claim 2 wherein the alkene or alkyne is a compound of the formula:

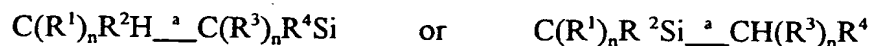
$$C(R^1)_nR^2 \text{--} \underline{a} \text{--} C(R^3)_nR^4$$
 wherein
 - a represents a double or triple bond;
 - when a is a triple bond, n is 0;
 - when a is a double bond, n is 1; and $R^1, R^2, R^3, \text{ and } R^4$ independently, are hydrogen, hydroxy, halo, cyano, isocyano, C_1-C_{18} alkoxy, C_1-C_{18} carboxy, C_1-C_{18} alkoxy carbonyl, primary, secondary or

tertiary amino, thiol, optionally substituted phosphino, borane (1) or borane (2), or C₁-C₁₈ alkylthioether or an optionally substituted C₁-C₁₈ alkyl, aryl, heteroaryl or vinyl group; and when R¹, R², R³ or R⁴ is a substituted group, the group is substituted with one or more substituents selected from the group consisting of hydroxy, halo, cyano, isocyano, C₁-C₁₈ alkoxy, C₁-C₁₈ carboxy, C₁-C₁₈ alkoxy carbonyl, primary, secondary or tertiary amino, thiol, optionally substituted phosphino, borane (1) or borane (2), or C₁-C₁₈ alkylthioether, halo C₁-C₁₈ alkyl, cyano C₁-C₁₈ alkyl, isocyano-C₁-C₁₈ alkyl, C₁-C₁₈ carbamido, or C₁-C₁₈ alkylthio group, a C₁-C₁₈ ferrocene substituent or another electron donor, or a biologically significant ligand selected from an antibody, a receptor protein, DNA or RNA, or a DNA or RNA analog capable of forming a double or triple stranded complex with DNA or RNA; or R² and R⁴, together with the carbon atoms to which they are attached, form a 5-, 6-, 7- or 8- membered ring.

6. The method of claim 1, claim 2 or claim 5 wherein the light source provides about 0.22 to about 44 mW/cm².

7. The method of claim 5 wherein the R² or R⁴ substituent on at least a portion of the alkene or alkyne is a substituted group wherein the substituent is hydroxy, carboxy, amino or thiol, said method further comprising the step of covalently coupling a biologically significant ligand to the silicon substrate through the substituent group.

8. A porous silicon substrate having a silicon surface comprising a covalently bound monolayer, said monolayer comprising a group of the formula:



wherein

Si is a surface silicon atom through which the substituted or unsubstituted vinyl or alkyl group is bonded to the silicon surface;

a represents a single or double bond;

when a is a double bond, n is 0;

when a is a single bond, n is 1; and

R¹, R², R³, and R⁴ independently, are hydrogen, hydroxy, halo, cyano, isocyano, C₁-C₁₈ alkoxy, C₁-C₁₈ carboxy, C₁-C₁₈ alkoxy carbonyl, primary, secondary or tertiary amino, thiol, optionally substituted phosphino, borane (1) or borane (2), or C₁-C₁₈

alkylthioether or an optionally substituted C₁-C₁₈ alkyl, aryl, heteroaryl or vinyl group; and when R¹, R², R³ or R⁴ is a substituted group, the group is substituted with one or more substituents selected from the group consisting of hydroxy, halo, cyano, isocyano, C₁-C₁₈ alkoxy, C₁-C₁₈ carboxy, C₁-C₁₈ alkoxycarbonyl, primary, secondary or tertiary amino, thiol, optionally substituted phosphino, borane (1) or borane (2), or C₁-C₁₈ alkylthioether, halo C₁-C₁₈ alkyl, cyano C₁-C₁₈ alkyl, isocyano-C₁-C₁₈ alkyl, C₁-C₁₈ carbamido, or C₁-C₁₈ alkylthio group, a C₁-C₁₈ ferrocene substituent or another electron donor, or a biologically significant ligand selected from an antibody, a receptor protein, DNA or RNA, or a DNA or RNA analog capable of forming a double or triple stranded complex with DNA or RNA; or R² and R⁴, together with the carbon atoms to which they are attached, form a 5-, 6-, 7- or 8- membered ring wherein the functionalized silicon surface retains at least 60% of the photoluminescence of the nonfunctionalized silicon surface.

9. The silicon substrate of claim 8 wherein a is a double bond, and R¹, R², R³, or R⁴ is an aryl or heteroaryl or phosphino metal chelating ligand and any metal complex of this metal chelating ligand.

10. The silicon substrate of claim 8 wherein at least a portion of the covalently bound R² or R³ group comprises a biologically significant ligand.

11. The silicon substrate of claim 8 wherein R² is H or C₁-C₄ alkyl, and R₃ comprises a biologically significant ligand.

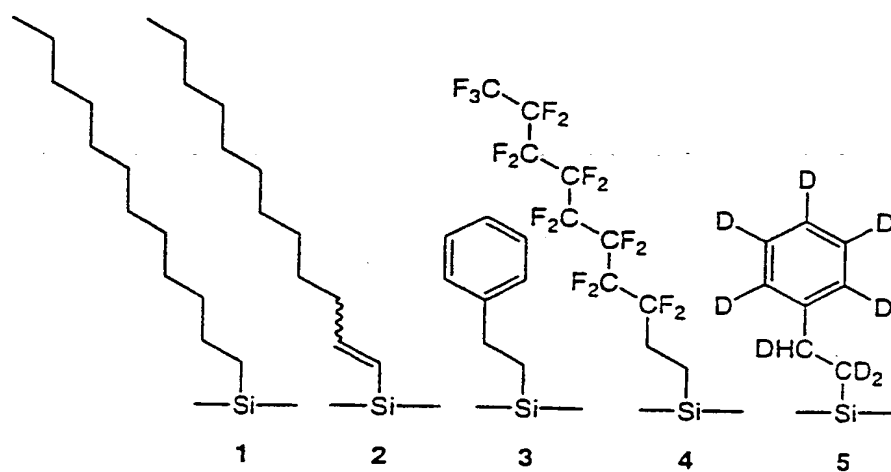


FIG. I

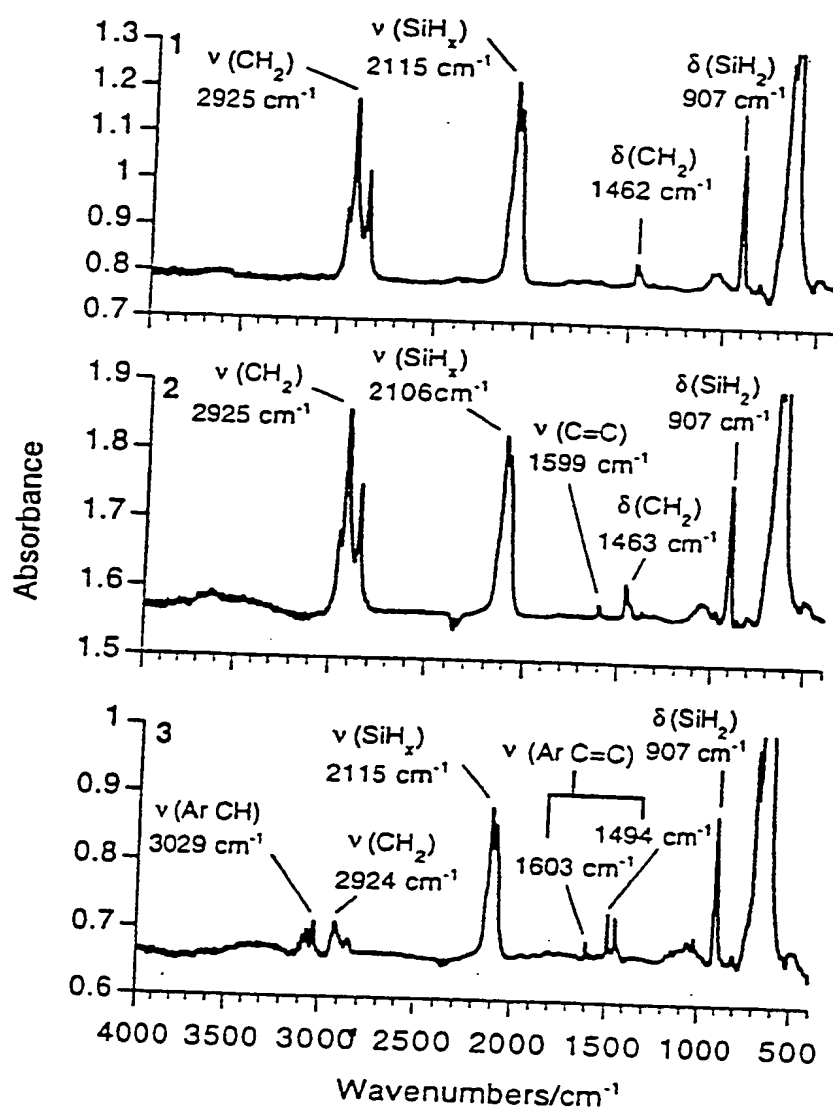


FIG. 2

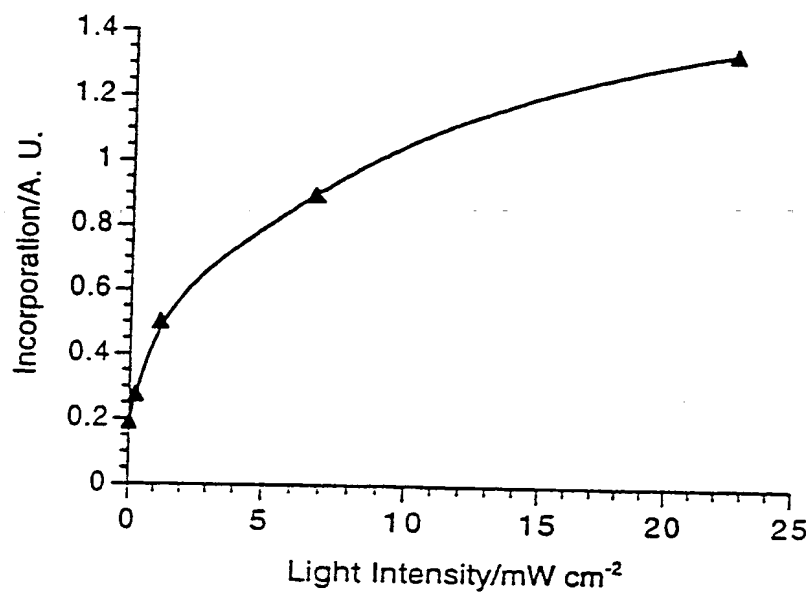


FIG. 3

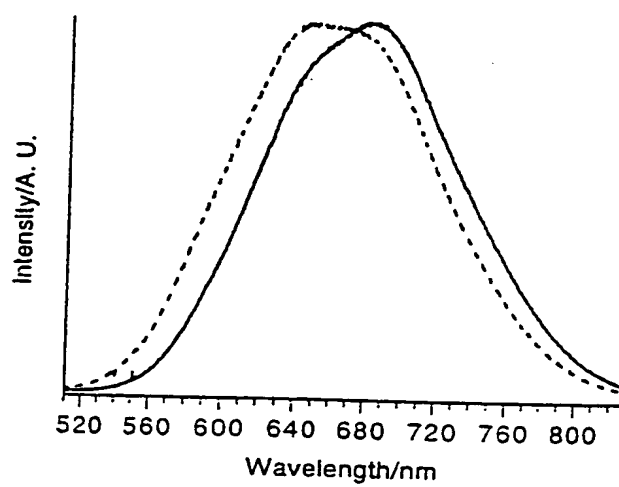
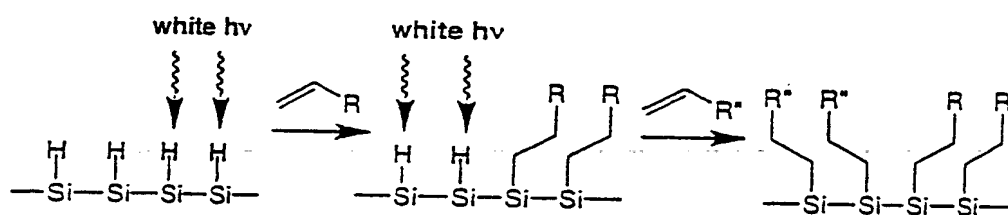
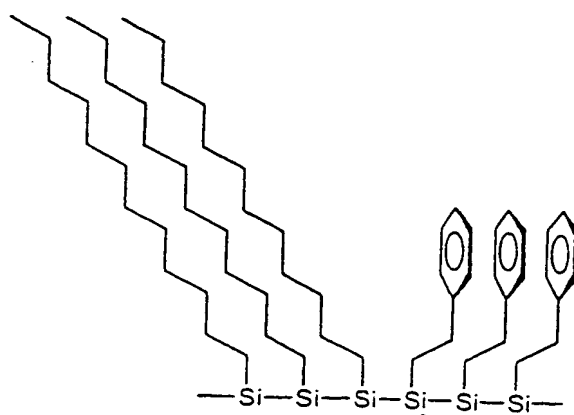


FIG.4

FIG. 5 *a*FIG. 5 *b*

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/25773

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :B32B 03/26

US CL :427/287, 444; 428/319.1, 409; 438/584

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 427/287, 444; 428/319.1, 409; 438/584

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
NONE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X -- A	US 5,561,304 A (CANHAM et al) 01 October 1996, see entire document.	1, 3, 5, 7, 8 ----- 2, 4, 9-11
A, P	US 5,834,378 A (KURTZ et al) 10 November 1998, see entire document.	1-11

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

Special categories of cited documents:			
A	document defining the general state of the art which is not considered to be of particular relevance	*T*	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
E	earlier document published on or after the international filing date	*X*	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
L	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*Y*	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
O	document referring to an oral disclosure, use, exhibition or other means	*&*	document member of the same patent family
P	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

13 JANUARY 2000

Date of mailing of the international search report

02 FEB 2000

Name and mailing address of the ISA/US
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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US99/25773

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 6
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.